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Abstract
PCC (precipitated calcium carbonate) and ground calcium carbonate have been widely used in alkaline papermaking. Unfortunately, although increasing filler level in papers can improve the paper properties such as brightness, opacity, stiffness gloss, smoothness, porosity, and printability, as well as decrease cost, some strength of the paper is negatively affected. In this research, needle-like aragonite was synthesized using $Ca(OH)_2$ and CO_2 as reactants in the presence of $MgCl_2$ and characterized with scanning electronic microscopy (SEM) and X-ray diffraction (XRD). The physical and optical properties of the paper handsheets containing these needle-like aragonite fillers were evaluated. Results indicated that tensile strength, Z-direction tensile strength and folding endurance of the paper were improved by the needle-like aragonite crystals compared to the paper using commercial PCC (precipitated calcium carbonate) as filler. The stiffness of the paper handsheet on the machine direction was increased, but no evident difference in the cross direction was found. The improvement of paper strength mainly resulted from the twining effect between the aragonite whiskers and paper fibers. The optical properties of the paper were slightly decreased with the use of the needle-like aragonites compared to commercial PCC. These results suggest that paper cost can be decreased by increasing the content of needle-like aragonite filler while paper strength will not be decreased compared to PCC filler.

Keywords
Calcium carbonate, filler, paper strength, polymorphism, aspect ratio, aragonite whisker

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1. Introduction

The incorporation of mineral fillers into paper stock prior to the formation of the sheet has been practiced since the eighth century. The paper industry utilizes fillers either to decrease the cost or to provide desired end-use properties of paper products. PCC (precipitated calcium carbonate) and ground calcium carbonate have been widely used in alkaline papermaking [1–4]. Although increasing filler level in papers can improve the paper properties such as brightness, opacity, stiffness gloss, smoothness, porosity, and printability, some physical properties are negatively affected.

It was thought that needle-like calcium carbonate filler might give excellent filler properties including bulk, brightness, opacity, and strength, as well as retention improvement [5–9]. Gill and Scott [10] found that PCC with aragonite or scalenohedral form is superior to the rhombohedral and ground calcium carbonates in optical properties at high loadings. Nanri [11] prepared various shapes of PCC in the form of rice-, spindle- and needle-like particles as paper fillers and found that both opacity and wire abrasion resistance of the paper were improved. Calcite is the most thermodynamically stable phase of calcium carbonate [12]. Aragonite is less thermodynamically stable and able to give needle-like morphology. Many factors can influence calcium carbonate polymorphism such as temperature [13, 14], solution pH [13, 15] and additives [7, 16]. Supersaturation degree of the solution was found to play an important role in the synthesis of metastable aragonite and vaterite [8, 9, 13, 17]. Too high supersaturation almost always results in calcite. Recently some simple techniques for the preparation of needle-like aragonite or aragonite whiskers have been developed [18–24]. In our previous study [25], sparingly dissoluble calcium salts were used as reactants to control the supersaturation degree and calcium carbonates with different polymorphisms were synthesized.

Inorganic whisker has been successfully used as reinforcement materials of composite materials. Beaudoin *et al.* [26] reported an improvement of aragonite micro fibers on flexural behavior of cement. Shang *et al.* [27] found that whisker aragonite was much better than calcite as composite filler. It is possible that paper fiber can twine aragonite whiskers together. Like mullite needle-like crystal of cement, this twining structure will improve strength of materials. Longer aspect ratio means stronger influence of twining whisker structure so more marked improvement of the paper strength. Therefore, it is of interest to see how these long needle-like fillers perform differently from small fillers in papermaking. In this study, we directly synthesized aragonite needle using $Ca(OH)_2$ and CO_2 in the presence of $MgCl_2$. Although a similar method for synthesis of aragonite has been reported in the literature [22–24], the effect of $MgCl_2$ on the polymorphisms has not been studied in detail. As filler of paper making the effects of needle-like aragonite on paper properties were also investigated.

2. Experimental

2.1. Calcium Carbonate Synthesis

The chemicals calcium hydroxide (95 wt%) and magnesium chloride hexahydrate were purchased from Aldrich, and carbon dioxide (Grade 2) was from Air Products.

In a typical synthesis, 9.209 g $MgCl_2 \cdot 6H_2O$ was first dissolved in 50 ml of deionized water (0.908 mol/l), then $Ca(OH)_2$ (2.205 g) was added to the solution, which was agitated till a stable pH was achieved. In this case, all of the $Ca(OH)_2$ would change into $Mg(OH)_2$. The concentration of excess $MgCl_2$ was 0.2811 mol/l. The suspension was heated to 70°C and was bubbled with a gaseous mixture of carbon dioxide in air. The rate of air injection was 360 ml/min. The reaction was stopped when the pH of the suspension was decreased to 7.5. Theoretically, no solid $Mg(OH)_2$ exists at this pH (the detailed discussion of the chemical equilibrium under these reaction conditions will be published separately). The suspension was filtered and washed with deionized water. The solid was then dried at 120°C for at least 4 h. In the synthesis for this research, the concentration of excess $MgCl_2$ varied from 0.0804 to 1.475 mol/l. The content of $Ca(OH)_2$ in the synthesis varied from 0.596 to 0.149 mol/l. The synthesis temperature of aragonite varied from 50°C to 70°C. The fractional pressure of CO_2 was between 13.6% and 24.3%. The final pH of the synthesis was in the range between 7.3 ± 0.2.

2.2. Preparation and Physical Properties Evaluation of Paper Handsheets

A mixture of 50% bleached hardwood pulp and 50% bleached softwood pulp, refined to 400 CSF were used for handsheet preparation. The pulp was diluted to 0.4 wt% before handsheets were made. A 2-ppm percol 175 (a cationic polyacrylamide flocculant, Ciba Specialty Chemicals, USA) solution was used as a retention aid. After the addition of fibers, needle-like aragonite and retention aid, the slurry was stirred for 20 s at 1000 rpm. A Moving Belt Drainage Tester (MBDT, built at IPST at Georgia Tech.) was used to prepare a handsheet with a target basis weight of 80 g/m^2. This equipment is appropriate to make a handsheet with fiber orientation similar to a paper machine. The detail about the equipment has been well addressed elsewhere [28]. As comparison, some handsheets were prepared from commercial PCC Albacar HO.

The wet handsheets were pressed at 50 psi for 5 min, dried at 105°C for 30 min, and then conditioned at 25°C and 50% RH overnight. The physical properties reported in this study were based on the average properties of nine handsheets. The statistical results, including average value, standard deviation, and error analysis of the physical properties, were calculated from 18 repeats. Physical properties, including tensile strength, Z-direction tensile and folding endurance were measured according to TAPPI standard methods. The PCC content in the handsheet was measured by EDTA titration method. Opacity and brightness of the handsheet were measured using a BNL-3 Opacimeter and a Micro TB-1C, respectively.

2.3. Characterization and Evaluation

A scanning electron microscope (JEOL, JSM-35C, Tokyo, Japan) was used to visualize the morphology of the calcium carbonate particles. XRD spectra of the products were measured using a PW1800 X-ray diffractometor (Philips, USA). A step size of 0.02° and scanning speed of 0.4 S per step were used to record spectra in the region from 20°–80° or 20°–32°. The polymorphic fraction of aragonite in crystalline calcium carbonate can be evaluated using the following equation [29] when no vaterite exists:

$$y = \frac{3.9S_a}{S_c + 3.9S_a},$$

where y is the calculated fraction of aragonite; S_c and S_a are the integrated intensities of X-ray diffraction spectra characteristic of calcite ($d_{(104)} = 3.304$ Å, $2\theta = 29.404°$) and aragonite ($d_{(111)} = 3.396$ Å, $2\theta = 26.213°$), respectively.

3. Results and Discussion

3.1. Synthesis and Structure Control of Needle-Like Aragonite

Theoretically, the synthesis of needle-like aragonite in this research dealt with three steps. First of all, $Ca(OH)_2$ will convert into $Mg(OH)_2$ in $MgCl_2$ aqueous solution because the solubility of $Ca(OH)_2$ is much higher than that of $Mg(OH)_2$:

$$Ca(OH)_2(s) + Mg^{2+}(aq) = Mg(OH)_2(s) + Ca^{2+}(aq) \tag{1}$$

The pH of the $Mg(OH)_2$ suspension is markedly lower than that of $Ca(OH)_2$ suspension. Then when CO_2 is bubbled to the system, the presence of $Mg(OH)_2$ will result in the following reaction:

$$Mg(OH)_2(s) + CO_2(g) = CO_3{}^{2-}(aq) + Mg^{2+}(aq) + H_2O \tag{2}$$

Calcium carbonate will form because of the reaction between Ca^{2+} and the $CO_3{}^{2-}$:

$$CO_3{}^{2-}(aq) + Ca^{2+}(aq) = CaCO_3(s) \tag{3}$$

In the synthesis, $CO_3{}^{2-}$ concentration follows equations as below:

$$CO_2(g) + H_2O = CO_3{}^{2-}(aq) + 2H^+(aq) \tag{4}$$

$$[CO_3{}^{2-}] = \frac{K_{a_1} K_{a_2} P_{CO_2}}{[H^+]^2} \tag{5}$$

where P_{CO_2} is the fractional pressure of CO_2 in the mixture gas and K_{a_1} and K_{a_2} are the acid constants of CO_2 and $HCO_3{}^-$, respectively. Equation (1) indicates that $[H^+]$ will increases because of the addition of $MgCl_2$. As a result, from (5) $[CO_3{}^{2-}]$ will be markedly decreased. The relative supersaturation of $CaCO_3$ in this synthesis was given by [30]:

$$\sigma = \Omega^{1/2} - 1 = [\alpha_{Ca^{2+}} \alpha_{CO_3{}^{2-}} / K_{spCaCO_3}]^{1/2} - 1, \tag{6}$$

where $\alpha_{Ca^{2+}}\alpha_{CO_3{}^{2-}}$ are the activities of related ions. K_{spCaCO_3} is the solubility product of $CaCO_3$. Solubility equilibrium of $Mg(OH)_2$ are given in (7) and (8). The concentration of $CO_3{}^{2-}$ in $Mg(OH)_2$ suspension can be calculated from (9), which is obtained from (5) and (8):

$$Mg^{2+}(aq) + 2OH^-(aq) = Mg(OH)_2(s) \tag{7}$$

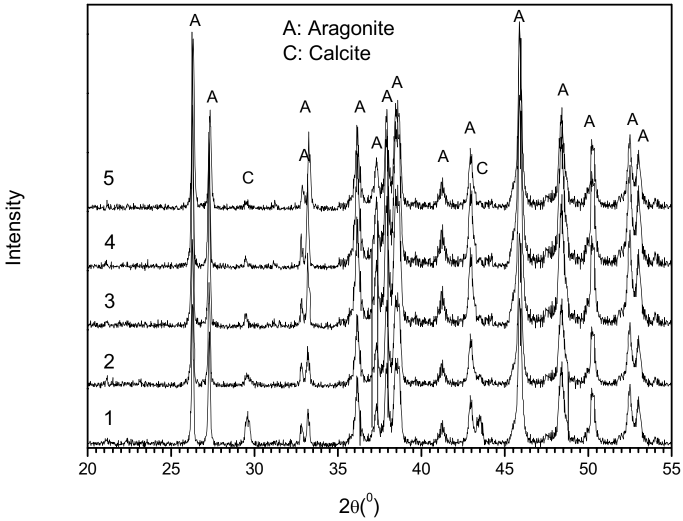
$$K_{spMg(OH)_2} = [Mg^{2+}][OH^-]^2 \tag{8}$$

$$[CO_3{}^{2-}] = \frac{P_{CO_2} K_{SPMg(OH)_2} K_{a_1} K_{a_2}}{[Mg^{2+}] K_w^2}, \tag{9}$$

where K_w is the ionization constant of water; $K_{SPMg(OH)_2}$ is the solubility product of $Mg(OH)_2$. From (9), we find that a high Mg^{2+} concentration and a low fractional pressure of CO_2 will result in a low $CO_3{}^{2-}$ concentration. In terms of (6), low $CO_3{}^{2-}$ concentration means low supersaturation of the synthesis. On the other hand, the addition of $MgCl_2$ will result in an increase of $[Ca^{2+}]$ because of the formation of $CaCl_2$ and $Mg(OH)_2$, which will increase supersaturation degree. The influence of $[H^+]$ on $[CO_3{}^{2-}]$ will be more marked than $[Ca^{2+}]$. As a total result, the additive $MgCl_2$ will decrease the degree of supersaturation of the calcium carbonate synthesis. Calcium carbonate possesses three kinds of crystal structures. Calcite is the thermodynamically stable phase and generally is in rhombohedral form. Aragonite and vaterite are metastable. Aragonite often shows a needle-like structure. It is well known that a lower degree of supersaturation favors the formation of aragonite. Therefore, the formation of aragonite whisker will be promoted by $MgCl_2$ due to the decrease of the degree of supersaturation.

The XRD diffraction patterns of calcium carbonate prepared in this way are given in Fig. 1. It can be seen that aragonite fraction increased with $[Mg^{2+}]$. This agrees very well with the above discussion, i.e., the increase of $[Mg^{2+}]$ will reduce the supersaturation σ, which favors the formation of aragonite. The influence of CO_2 fractional pressure on polymorphism of product calcium carbonate is given in Fig. 2. In terms of the results of Fig. 1, $MgCl_2$ in those samples of Fig. 2 was in great excess so that a high fraction of aragonite can be obtained. A synthesis temperature of 70° was used in Fig. 2, which favors the formation of long aragonite needles and will be discussed below. It can be seen that aragonite content decreased with the increase of CO_2 fractional pressure, which can also be ascribed to the influence of the CO_2 fractional pressure on supersaturation degree of the synthesis. Comparing with the effect of $MgCl_2$ concentration, CO_2 showed a weak influence on the polymorphism. These results suggest that polymorphism of aragonite synthesis can be controlled to some extent with $MgCl_2$ concentration and CO_2 fractional pressure.

SEM images of the needle-like aragonites, prepared with different $MgCl_2$ concentrations are given in Fig. 3. Some needle-like aragonite with a length between 40 and 120 μm can be found. This size is much bigger than the diameter of calcite PCC and is smaller than that of wood fiber. The aspect ratio of those aragonite needles decreases as $MgCl_2$ concentration increases. A higher $MgCl_2$ concentration means



1: excessive $MgCl_2$ 0.0804 mol/L; 2: excessive $MgCl_2$ 0.201 mol/L
3: excessive $MgCl_2$ 0.495 mol/L; 4: excessive $MgCl_2$ 0.985 mol/L
5: excessive $MgCl_2$ 1.475 mol/L

Figure 1. Effect of $MgCl_2$ concentration on polymorphism of calcium carbonate.

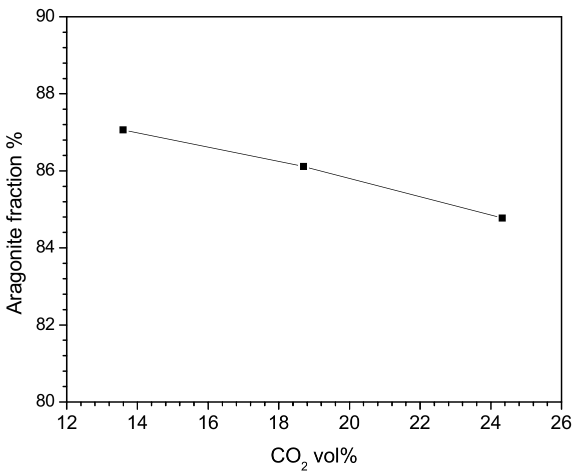


Figure 2. Effect of CO_2 concentration on calcium carbonate polymorphism. 2.205 g $Ca(OH)_2$ was added to 200 ml of $MgCl_2$ solution. Excess $MgCl_2$ concentration: 0.2811 mol/l. Then the suspension was bubbled with CO_2 mixture gas at 70°C to a pH of 7.3 ± 0.2.

a lower supersaturation degree so slower growth rate of the aragonite. This result means that a lower degree of supersaturation is not beneficial to the formation of needle-like aragonite with higher aspect ratio. SEM images of the products, prepared at different temperatures are given in Fig. 4. Comparing with Fig. 4(c) some small particles in Fig. 4(b) can be found, which should be calcite. These results indi-

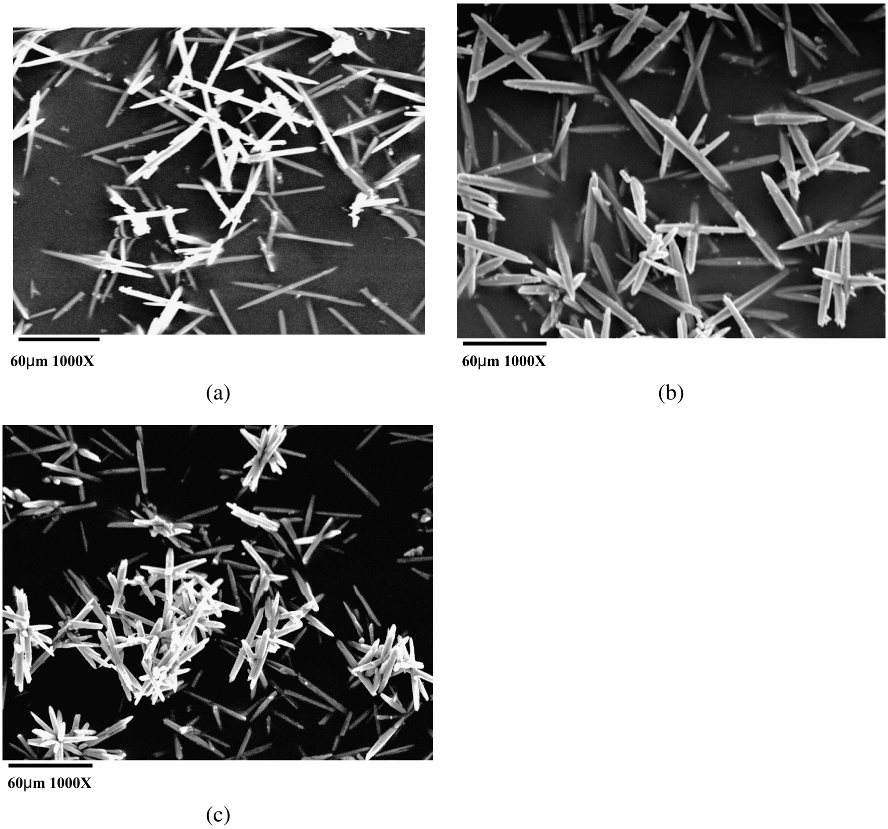
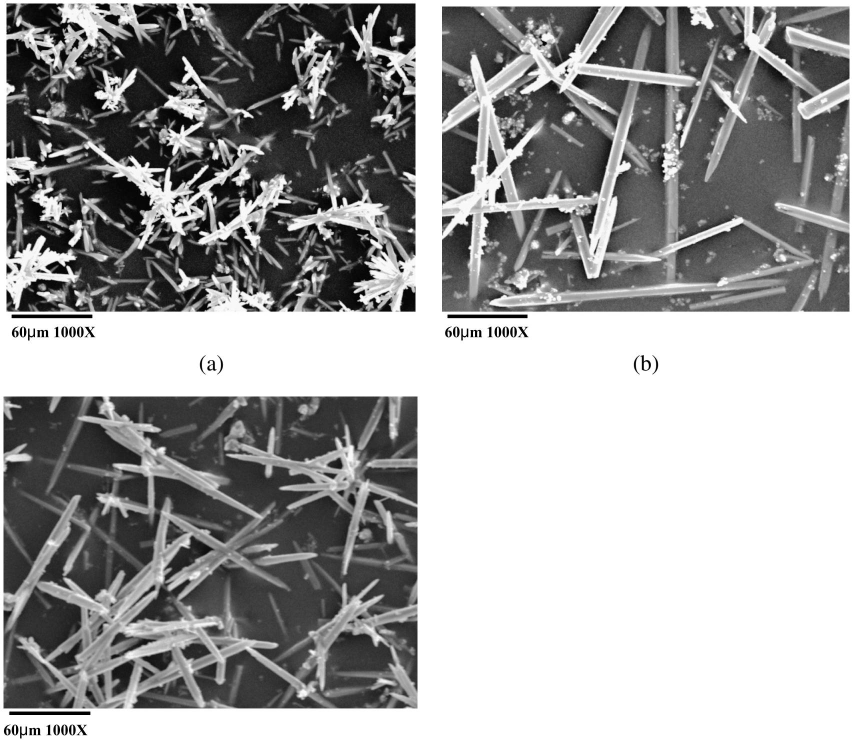


Figure 3. Effect of $MgCl_2$ concentration on the aspect ratio of calcium carbonate: (a) excess $MgCl_2$: 0.0804 mol/l aspect ratio = 16.4 ± 0.90; (b) excess $MgCl_2$: 0.201 mol/l aspect ratio = 8.72 ± 0.47; (c) excess $MgCl_2$: 0.495 mol/l aspect ratio = 7.73 ± 0.63. 2.205 g $Ca(OH)_2$ was added to 50 ml $MgCl_2$ solution with agitation at room temperature. Then the suspension was bubbled with 18.70 vol% CO_2 in air at 70°C to a pH of 7.3 ± 0.2.

cate that higher temperature, such as 70°C favors the formation of long needle-like aragonite. All of these results demonstrate that the structure of needle-like aragonite can be controlled with reactant concentration and reaction conditions.

3.2. Properties of the Paper Filled with Needle-Like Aragonite

Tensile strength of the paper filled with needle-like aragonite was compared with that containing commercial PCC and the results are given in Fig. 5. Apparently, all samples filled with aragonites show higher tensile strength. Results of the Z-direction tensile strength (ZDT) and folding endurance of the paper are given in Figs 6 and 7, respectively. A higher folding endurance was also observed for the paper filled with the needle-like aragonite. All of these results suggest that needle-like aragonite indeed improve paper strength.



(a) (b) (c)

Figure 4. Effect of temperature on aspect ratio of needle-like aragonite. (a) Aragonite synthesis temperature 50°C aspect ratio = 9.12 ± 1.15; (b) aragonite synthesis temperature 60°C aspect ratio = 14.14 ± 1.14; (c) aragonite synthesis temperature 70°C aspect ratio = 10.33 ± 0.72. 2.205 g $Ca(OH)_2$ was added to 50 ml of $MgCl_2$ solution with agitation at room temperature. Excess $MgCl_2$ concentration: 0.2219 mol/l. Then the suspension was bubbled with 18.70 vol% CO_2 in air to a pH of 7.3 ± 0.2.

The stiffness of paper handsheets on machine direction with different fillers is given in Fig. 8, which reveals a significant enhancement of the paper filled with needle-like aragonite. We also found, though this is not shown in this paper, that the cross direction of the handsheet did not show evident enhancement. These results suggest that the needle-like aragonite crystals possess alignment array along machine direction. The improvement of paper strength mainly resulted from the twining effect between the aragonite whiskers and paper fibers. There exists a wide error bar in the measurement of handsheet stiffness. Therefore, evident improvement of the stiffness by needle-like aragonite can only be found at filler content above 10%. Opacity comparison of those papers is given in Fig. 9. The needle-like aragonite was found having a lower opacity because of its large size. These results are different from that of Gill and Scott [10] where PCC with aragonite form was found to be superior to the rhombohedral and ground calcium carbonates in optical properties at high loadings. The different behaviors might be ascribed to the different particle size and the loading amount of aragonite.

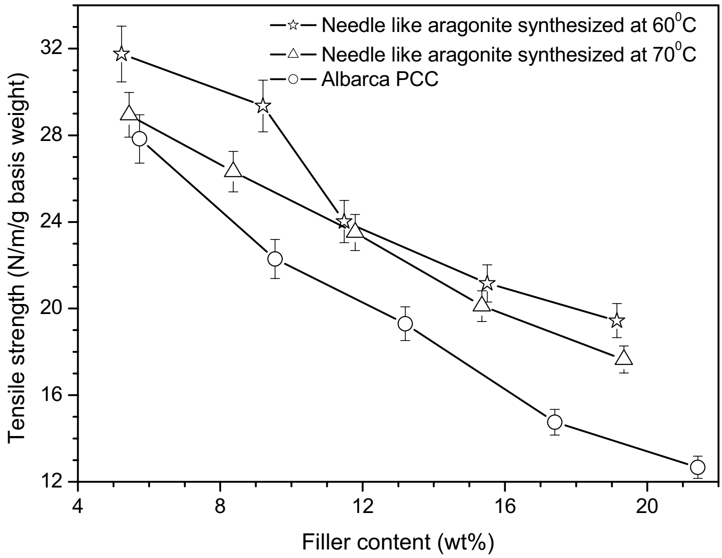


Figure 5. Effect of needle-like aragonite on tensile strength of paper. 8.82 g $Ca(OH)_2$ was added to 200 ml $MgCl_2$ solution with agitation at room temperature. Excess $MgCl_2$ concentration: 0.2811 mol/l. Then the suspension was bubbled with 18.70 vol% CO_2 in air to a pH of 7.3 ± 0.2.

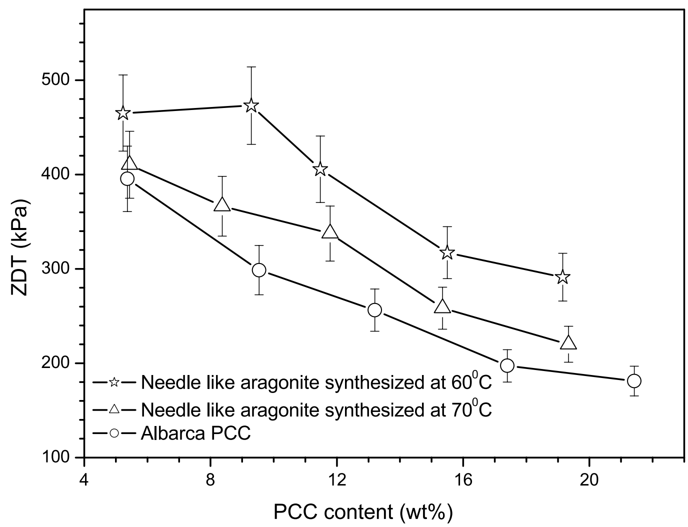


Figure 6. Influence of needle-like aragonite on *Z* direction tensile of paper. 8.82 g $Ca(OH)_2$ was added to 200 ml $MgCl_2$ solution with agitation at room temperature. Excess $MgCl_2$ concentration: 0.2811 mol/l. Then the suspension was bubbled with 18.70 vol% CO_2 in air to a pH of 7.3 ± 0.2.

4. Conclusions

Needle-like aragonites were synthesized using $Ca(OH)_2$ and CO_2, as raw materials in the presence of $MgCl_2$. The polymorphism of the product strongly depends on

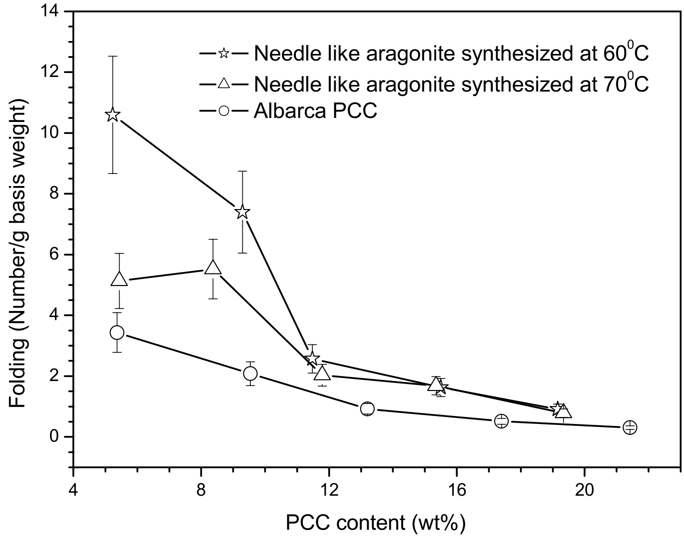


Figure 7. Effect of needle-like aragonite on the folding endurance of paper. 8.82 g $Ca(OH)_2$ was added to 200 ml $MgCl_2$ solution with agitation at room temperature. Excess $MgCl_2$ concentration: 0.2811 mol/l. Then the suspension was bubbled with 18.70 vol% CO_2 in air to a pH of 7.3 ± 0.2.

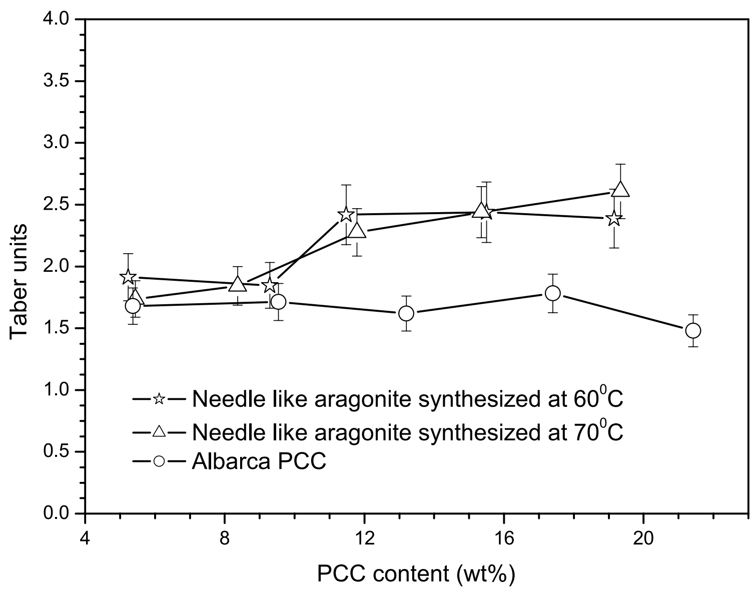


Figure 8. Effect of needle-like aragonite on stiffness of paper on machine direction. 8.82 g $Ca(OH)_2$ was added to 200 ml $MgCl_2$ solution with agitation at room temperature. Excess $MgCl_2$ concentration: 0.2811 mol/l. Then the suspension was bubbled with 18.70 vol% CO_2 in air to a pH of 7.3 ± 0.2.

$MgCl_2$ concentration. Fractional pressure of CO_2, however, has less impact on the polymorphism than Mg^{2+} concentration. Tensile strength, the Z-direction tensile

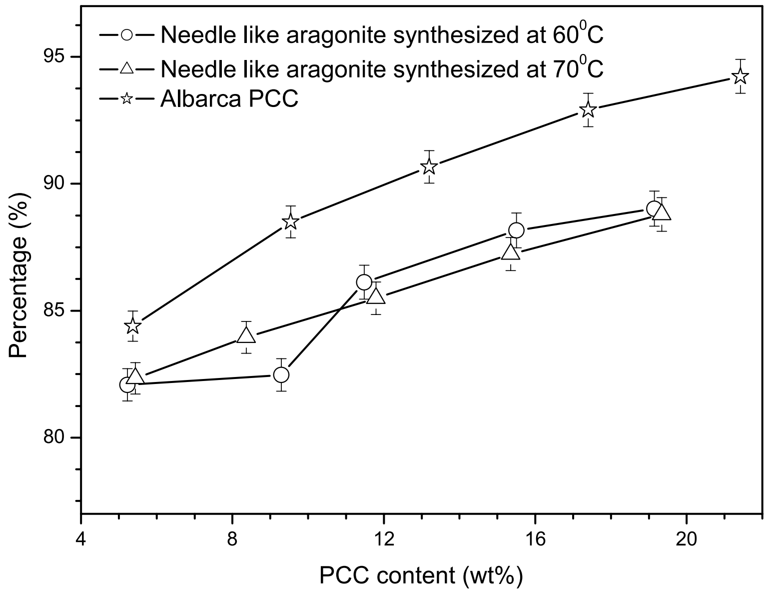


Figure 9. Influence of needle-like aragonite on the opacity of paper. 8.82 g $Ca(OH)_2$ was added to 200 ml $MgCl_2$ solution with agitation at room temperature. Excess $MgCl_2$ concentration: 0.2811 mol/l. Then the suspension was bubbled with 18.70 vol% CO_2 in air to a pH of 7.3 ± 0.2.

strength and folding endurance of paper were markedly improved by needle-like aragonite prepared as described in this paper. The stiffness of the paper in the machine direction was evidently increased. This result suggests that the needle-like aragonite aligns itself along the machine direction. The improvement of paper strength mainly resulted from a twining effect between the aragonite whiskers and paper fibers. The opacity of the paper sheets filled with needle-like aragonite was decreased comparing to Albacar HO PCC.

References

1. Y. Xu and Y. Deng, Retention of precipitated calcium carbonate in old corrugated container furnishes, *Tappi J.* **82**, 121–126 (1999).
2. T. Enomae and K. Tsujino, Application of spherical hollow calcium carbonate particles as filler and coating pigment, in: *TAPPI Coating and Graphic Arts Conf. Trade Fair*, pp. 505–525 (2002).
3. T. Haller, L. Stryker and A. Janson, PCC application strategies to improve papermaking profitability. Part I: Thick stock precipitated calcium carbonate addition, in: *TAPPI Papermakers Conf.*, pp. 1119–1128 (2001).
4. K. Patrick, Quality, cost benefits spur increased GCC use by paper mills worldwide, *Pulp and Paper* **71**, 81–83 (1997).
5. V. K. Mathur, International Patent Application, WO 01/14274 A1 (2001).
6. T. Kazuto, K. Kiyoshi, N. Yasunori and O. Yasuhiro, US Patent 6,190,633 (2001).
7. J. Arika, M. Takitani, K. Mitarai and K. Yamamoto, US Patent 4,157,379 (1979).
8. Y. Ota, N. Goto, I. Motoyama, T. Iwashita and K. Nomura, US Patent 4,824,654 (1989).

9. G. H. Fairchild and R. L. Thatcher, US Patent 6,071,336 (2000).
10. T. Gill and W. Scott, The relative effects of different calcium carbonate filler pigments on optical properties, *Tappi J.* **70**, 93–99 (1987).
11. Y. Nanri, On-site production of high quality precipitated calcium carbonate using the causticization step in kraft pulping process, *Japan Tappi J.* **55**, 103–110 (2001).
12. G. Wolf and C. Gunther, Thermophysical investigations of the polymorphous phases of calcium carbonate, *J. Thermal Anal. Calorimetry* **40**, 687–698 (2001).
13. C. Y. Tai and F. B. Chen, Polymorphism of $CaCO_3$ precipitated in a constant-composition environment, *AIChE J.* **44**, 1790–1798 (1998).
14. A. G. Xyla, E. Giannimnaras and P. G. Koutsoukos, Precipitation of calcium carbonate in aqueous solutions, *Colloids Surfaces* **53**, 241–255 (1991).
15. D. Kraji, L. Brecevi and A. E. Nielsen, Vaterite growth and dissolution in aqueous solution I. Kinetics of crystal growth, *J. Cryst. Growth* **104**, 793–800 (1990).
16. F. C. Meldrum and S. T. Hyde, Morphological influence of magnesium and organic additives on the precipitation of calcite, *J. Cryst. Growth* **231**, 544–558 (2001).
17. G. H. Fairchild and R. L. Thatcher, US Patent 6,022,517 (2000).
18. E. He, W. Shang and S. Chen, Effects of phosphate ion on the growth of aragonite whisker in heterogeneous precipitation from suspension of $Ca(OH)_2$, *Xiyou Jinshu Cailiao Yu Gongcheng/Rare Metal Materials and Engng* **29**, 398–405 (2000).
19. W. Shang, Q. Liu and S. Chen, Synthesis of aragonite whiskers using gas-liquid system, *Hsi-An Chiao Tung Ta Hsueh/ J. Xi'an Jiaotong University* **33**, 10–17 (1999).
20. W. Shang, Q. Liu, W. Chen, B. Liu and L. Chu, Synthesis and application of aragonite whisker, in: *Intl. Sympos. on Elect. Insul. Mater. Proc.* E3–5, pp. 595–598 (1998).
21. Q. Liu, W. Shang, B. Liu, W. Chen and S. Chen, Preparation of aragonite carbonation process, *Hsi-An Chiao Tung Ta Hsueh/J. Xi'an Jiaotong University* **33**, 17–23 (1999).
22. Y. Ota, S. Inui, T. Iwashita, T. Kasuga and Y. Abe, Preparation of aragonite whiskers, *J. Amer. Ceram. Soc.* **78**, 1983–1984 (1995).
23. Y. Ota, S. Inui, T. Iwashita, T. Kasuga and Y. Abe, Preparation conditions for aragonite whiskers by carbonation process, *J. Ceram. Soc. Japan* **104**, 196–200 (1996).
24. L. Zhang, Z. Zhang, H. Guo and Y. Yu, Preparation of uniform aragonite whisker by carbonation process, *J. Sichuan Univ. (Engng Sci. Ed.)* **34**, 46–52 (2002).
25. Z. S. Hu and Y. L. Deng, Supersaturation control in aragonite synthesis using sparingly dissoluble calcium salts as reactants, *J. Coll. Interf. Sci.* **266**, 359–365 (2003).
26. J. J. Beaudoin, P. Gu, P. and W. Lin, Flexural behavior of cement systems reinforced with high aspect ratio aragonite micro-fibres, *Cement Concrete Res.* **26**, 1775–1777 (1996).
27. W. Shang, Q. Liu, E. He and S. Chen, Study on properties of polymers packed by aragonite whisker, *Proc. IEEE Intl Conf. Prop. Appl. Dielectric Mater.* **1**, 431–434 (2000).
28. S. Karrila, J. Champine and D. White, Pulsating forming at headbox consistency in bench scale provides close imitation of a single-wire machine — or how to tune a lab device for desired web structure, in: *TAPPI Spring Technical Conf. and Exhibit*, Chicago, IL, USA, pp. 599–605 (2003).
29. N. Wada, M. Okazaki and S. Tachikawa, Effects of calcium-binding polysaccharides from calcareous algae on calcium carbonate polymorphs under conditions of double diffusion, *J. Cryst. Growth* **132**, 115–121 (1993).
30. E. Dalas, P. Klepetsanis and P. Koutsoukos, Overgrowth of calcium carbonate on poly(vinyl chloride-co-vinyl acetate-co-maleic acid), *Langmuir* **15**, 8322–8327 (1999).